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13. ABSTRACT (Maximum 200 words) Complexation of bis(8-hydroxyquinoline)-substituted tetraaza-15-crown-5 (1) (see our Technical Report No. 6) with Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} was evaluated potentiometrically in aqueous solution (0.10 M Me_4NCl) at 25°C. Ligand 1 formed very stable complexes with these metal ions. The UV-Vis spectra of 1 and its complexes were examined in an aqueous acetic acid buffer solution (pH 4.7). The 1- Cu^{2+} complex provided a new absorption band at 258 nm.				
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**Preliminary Complexation Studies of Bis(8-hydroxyquinoline)-substituted
Tetraaza-15-crown-5 with Various Metal Ions**

by

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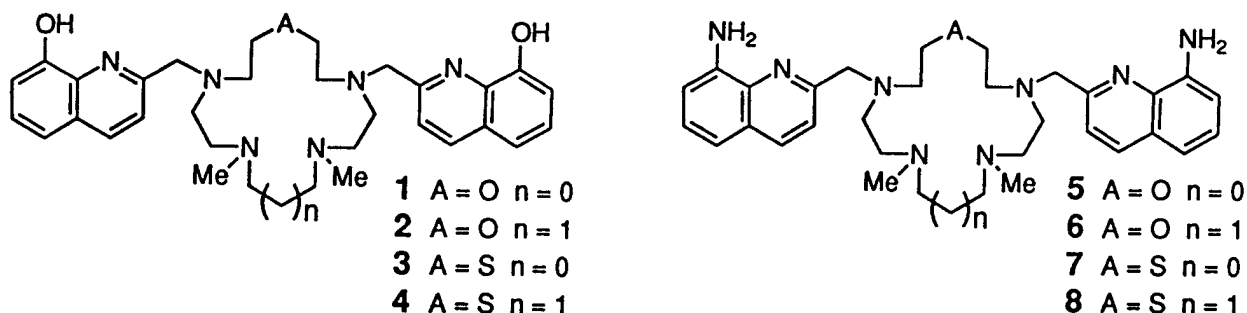
PRELIMINARY COMPLEXATION STUDIES OF
BIS(8-HYDROXYQUINOLINE)-SUBSTITUTED TETRAAZA-
15-CROWN-5 WITH VARIOUS METAL IONS

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Results and Discussion

A series of new 8-hydroxyquinoline- and 8-aminoquinoline-substituted tetraaza-15-(-16)-crown-5 ethers (1-4 and 5-8, respectively) have been prepared in our laboratory.¹ These new ligating agents were designed to selectively bind transition and post-transition metal ions with a concomitant modulation in the absorption and fluorescent spectra of the compounds. This report gives a preliminary account of the complexation of ligand 1 with various metal ions.



Protonation and Complexation Studies of Ligand 1. Protonation constants of 8-hydroxyquinoline-containing tetraazacrown ether 1 and stability constants for the interactions of 1 with Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were determined by a potentiometric titration technique² at 25°C in aqueous solution. The ionic strength was kept constant with 0.10 M tetramethylammonium chloride. The overall reactions are expressed by the general equation:



where M is the metal ion and L is the ligand. The overall equilibrium constant can be defined as

$$\beta_{pqr} = [\text{M}_p\text{H}_q\text{L}_r^{(2p+q-2r)}] / [\text{M}^{2+}]^p [\text{H}^+]^q [\text{L}^{2-}]^r \quad (2)$$

The values of the protonation constants of the ligands and stability constants of the metal ion complexes ($\log \beta_{pqr}$) are listed in Tables 1 and 2, respectively.

Four protonation constants can be calculated for compound 1. The first two protonation constants ($\log K_1 = 9.55$ and $\log K_2 = 7.30$ (16.85 - 9.55), Table 1) and the last two constants

Table 1. Logarithms of Protonation Constants of Macrocyclic Ligand 1 in Aqueous Solution (0.10 M Me₄NCl) at 25.0 °C

Reaction	log β
$H^+ + L^{2-} \rightleftharpoons HL^-$	9.55 ± 0.05
$2H^+ + L^{2-} \rightleftharpoons H_2L$	16.85 ± 0.08
$3H^+ + L^{2-} \rightleftharpoons H_3L^+$	19.87 ± 0.09
$4H^+ + L^{2-} \rightleftharpoons H_4L^{2+}$	21.31 ± 0.14

hydroxyquinoline portion and the last two forming a neutral complex with a divalent cation which may be coordinated by both the 8-hydroxyquinolines and the macroring.

Data in Table 2 show that each metal ion studied forms several types of complexes with the ligand. The 1:1 complexes ML ($p = 1, q = 0, r = 1$ in eq. 1) and M(OH)L⁻ ($p = 1, q = -1, r = 1$) are observed in each case. The complexes of ligand 1 with Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ are very stable in aqueous solution. The large stability constants (log $\beta_{ML} > 12$ and log $\beta_{MHL} > 15$) are shown in Table 2. The most stable complexes were observed for Cu²⁺. The values of log β_{CuL} and log β_{CuHL} are 15.5 and 18.6, respectively. Cd²⁺ also forms very stable complexes with ligand 22 (log $\beta_{CdL} = 15.3$ and log $\beta_{CdHL} = 17.5$). Therefore, not only the fully deprotonated form of 22 (L²⁻) but also the monoprotonated ligand (HL⁻) forms very stable complexes with the metal ions studied (except for Co²⁺). In the case of Co²⁺, the complex CoHL⁺ was not detected. However, Co²⁺ forms a 1:2 (M:L) complex with 1 (log $\beta_{CoL_2} = 20.2$). A dinuclear complex with Cu²⁺, Cu₂L²⁺, was also observed. The equilibrium constants of the complexes containing hydrolysis products of the metal ions, M(OH)L⁻, range from 6.44 (log $\beta_{Co(OH)L}$) to 9.62 (log

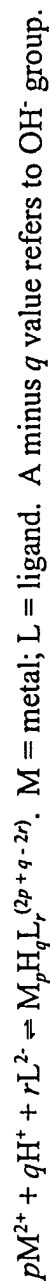
(log $K_3 = 3.02$ and log $K_4 = 1.44$) are close to each other. A large decrease in protonation constants is seen between the second and the third protonation steps. Since the first protonation constant of 1 (log $K_1 = 9.55$) is hydroxyquinoline (9.65 at 25 °C, $\mu = 0.1$),³ the first two protonation constants of 1 are due to protonation of OH groups of the 8-

Table 2. Overall Stability Constants^a of Metal Ion Complexes with Macrocyclic Ligand 1 in Aqueous Solution (0.10 M Me₄NCl) at

25.0 °C

			$\log \beta_{pqr}$				
<i>p</i>	<i>q</i>	<i>r</i>	Cu ²⁺	Co ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺
1	0	1	15.52 ± 0.08	12.34 ± 0.04	13.46 ± 0.03	12.41 ± 0.03	15.33 ± 0.02
1	1	1	18.55 ± 0.12		16.15 ± 0.18	15.55 ± 0.09	17.50 ± 0.05
1	-1	1	8.53 ± 0.19	6.44 ± 0.06	7.49 ± 0.12	6.49 ± 0.05	9.62 ± 0.07
2	0	1	18.92 ± 0.22				
1	0	2		20.19 ± 0.06			
1	-2	1			-3.59 ± 0.25		

^aThe equilibria of the reactions are defined by the general equation:



$\beta_{\text{Cd}(\text{OH})\text{L}}$). The Ni^{2+} forms a second type of hydrolysis complex, $\text{Ni}(\text{OH})_2\text{L}^{2-}$, which has a very low equilibrium constant (Table 2).

UV-Visible spectra. The UV spectra of free and complexed ligand 1 are shown in Figures 1 and 2. The free 1 has an absorption maximum at 244 nm. Upon addition of Cu^{2+} , a new peak develops at 258 nm (Figure 1). Other metal ions (Zn^{2+} , Pb^{2+} , Cd^{2+} , Ag^+ , Hg^{2+} , Co^{2+} , and Ni^{2+}) were also titrated with 1, but none produced a new peak or significantly interfered with the new 1- Cu^{2+} complex peak at 258 nm (Figure 2). Thus, the 258 nm peak for the 1- Cu^{2+} complex could be used for sensing purposes.

Experimental Section

Determination of Protonation and Stability Constants. The protonation and stability constants were determined by potentiometric titration in aqueous solution at 25 °C. The titrations were carried out at a constant ionic strength of 0.10 M Me_4NCl using an automatic microprocessor-controlled potentiometric titrator.⁴ Temperature was controlled within ± 0.1 °C using a jacketed cell through which water from a constant-temperature bath was circulated. Potentials to within ± 0.1 mV were measured using an Orion Model 701A Digital Ion Analyzer in conjunction with a Cole-Parmer combination electrode (Ag/AgCl reference cell). The electrode was calibrated by two precision buffer solutions, pH 4.000 ± 0.002 and 7.000 ± 0.002 at 25.0 °C (Cole-Parmer). Calculations were performed with the SUPERQUAD program⁵ using an IBM computer. Compound 1 was used as its adduct with HCl ($1 \cdot 6\text{HCl}$) which had good solubility in aqueous solution (0.01 M).

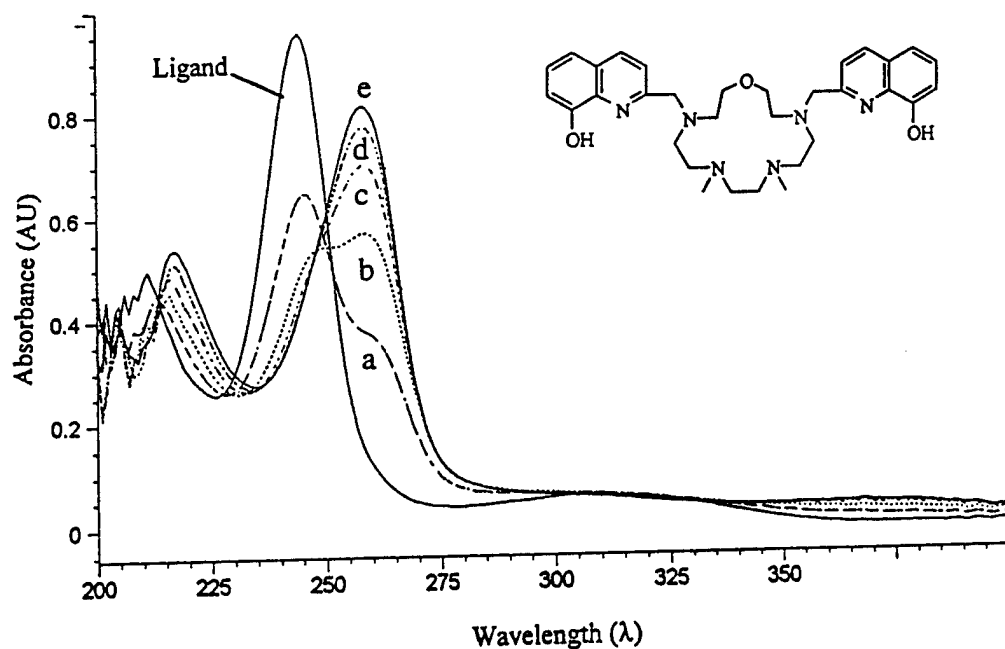


Figure 1. UV-visible spectra of free 1 and its Cu^{2+} complexes in an aqueous buffered solution. $[1] = 0.977 \times 10^{-5} \text{ M}$, $[\text{buffer}] = 5.0 \times 10^{-2} \text{ M}$ acetic acid ($\text{pH} = 4.7$). The labels a - e indicate 1 - 5 equivalents of Cu^{2+} added to the ligand successively.

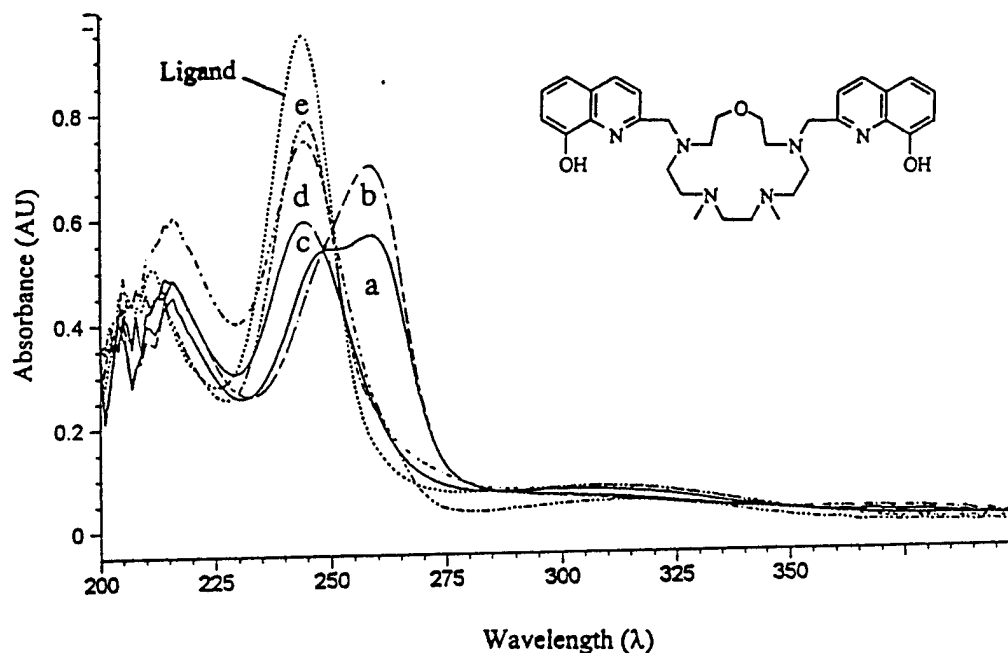


Figure 2. UV-visible spectra of free and complexed 1 in acetic acid buffer solution ($\text{pH} = 4.7$). (a and b) Cu^{2+} (1 and 2 equivalents, respectively), (c) Zn^{2+} , (d) Pb^{2+} , and (e) Cd^{2+} (2 equivalents each). $[1] = 0.977 \times 10^{-5} \text{ M}$ and $[\text{buffer}] = 5.0 \times 10^{-2} \text{ M}$ acetic acid.

UV-visible Spectral Measurements. UV-visible spectra were recorded at 23 ± 1 °C in a 1-cM quartz cell using a Hewlett-Packard 8452A Diode Array spectrophotometer. Both ligand and metal ions were prepared in aqueous acetic acid buffer (pH = 4.7). Concentrations of acetic and sodium acetate were 5.00×10^{-2} M and 5.00×10^{-2} M, respectively, and concentration of ligand 1 was 1.00×10^{-5} M. The metal ion concentrations were 1-5 times the ligand concentration.

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